



Trade Science Inc.

ISSN : 0974 - 7443

Volume 7 Issue 1

CHEMICAL TECHNOLOGY

An Indian Journal

Full Paper

CTAIJ 7(1) 2012 [24-28]

Adjusting critical parameters for designing the sulfur recovery units (SRUs)

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Received: 4th March, 2012 ; Accepted: 4th April, 2012

ABSTRACT

The modified Claus process is commonly used in oil refining and gas processing to recover sulfur and destroy contaminants formed in upstream processing. In oil refining, in addition to the typical modified Claus plant feed of H₂S and CO₂, NH₃, CS₂, and COS are also often present or formed. These contaminants pose a risk of poisoning the catalyst beds and plugging off downstream equipment, as well decreasing the overall achievable sulfur recovery. In this paper, the parameters that may affect adjusting the temperature of furnace and converters will be discussed. These process parameters are important in designing a new Claus sulfur recovery plant. For this purpose, a typical sulfur recovery unit is analyzed and the main process temperatures are achieved.

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KEYWORDS

Furnace;
Converter;
Sulfur recovery unit.

INTRODUCTION

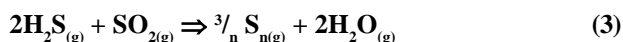
The Claus process continues to be the most widely used process for the conversion of H₂S to sulfur^[1]. The task of Claus processes is to recover elemental sulfur from hydrogen sulfide and, more generally, from byproduct gases originating from physical and chemical gas and oil treatment units in refineries, natural gas processing, and gasification plants, to quote a few^[2]. They consist of a thermal reaction furnace, a waste heat boiler, and a series of catalytic reactors (Converters) and condensers (Figure 1). The reactions occurring in the furnace are numerous, and several authors have attempted to delineate the important ones^[3-6]. The overall reaction characterizing the process is as follows^[2]:



In the first step or thermal stage, one-third of the H₂S is completely oxidized to SO₂ in the reaction furnace, located at the front end of plant. A benefit that also occurs is the production of significant quantities of elemental sulfur (S₂) from the thermal decomposition of H₂S. In fact, the sulfur produced in the furnace is 50-60% of the total sulfur condensed in the plant. The main H₂S oxidation reaction is^[7],



The reaction furnace is followed by the waste heat boiler (WHB), where heat is recovered by cooling the furnace product gases^[7]. In the second step or the catalytic stage, unreacted H₂S is then combined with SO₂, produced via eq. 2, over an alumina catalyst to form elemental sulfur in fixed bed reactors by the following reaction^[7,8],



High conversions for this exothermic, equilibrium-limited reaction call for low temperatures, the use of which, however, leads to low reaction rates, so that a catalyst must be employed. Even so, high sulfur yields still necessitate a multistage process with interstage cooling and sulfur condensation^[8].

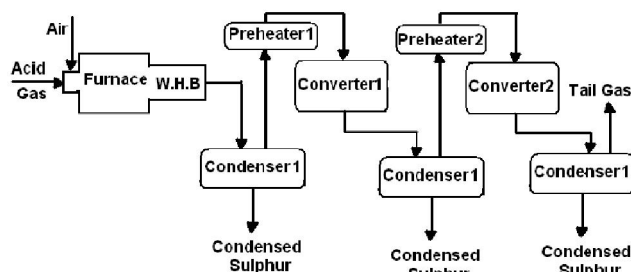


Figure 1 : The configuration of a typical Claus unit

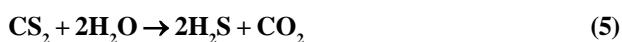
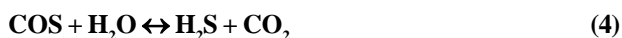
Sulfur formed in each stage of the Claus plant is condensed and recovered to achieve maximum conversion in the catalytic reactors. The unrecovered sulfur, in elemental or combined form (H_2S , COS , CS_2), is combusted to SO_2 in the tail gas incinerator which is then emitted to the atmosphere. Tail gas clean-up units are added sometimes prior to incineration to increase the sulfur recovery and minimize emissions^[7].

One of the furnace functions is destruction of any contaminants which may foul downstream equipment. In oil refinery operations, NH_3 is formed as a byproduct which is then directed to the sulfur recovery facility for destruction^[5]. Incomplete pyrolysis or combustion of NH_3 in the furnace results in NH_3 and NO carryover into the catalyst beds. Ammonia can form ammonium salts, which can plug or foul the catalyst beds, other equipment, or piping. Although the formation of SO_3 occurs in the catalyst bed regardless of the presence of NO , the presence of NO in the beds acts as a catalyst for the conversion of SO_2 to SO_3 , which in turn causes catalyst sulfation^[9]. Of the primary causes of catalyst activity loss, catalyst sulfation is regarded as the most significant^[10]. It is therefore critical to convert as much of the NH_3 to N_2 , H_2 , and H_2O as possible.

For ammonia destruction, an empirical rule of thumb that is generally agreed with in industry is that temperatures greater than 1200-1250 °C are required^[5]. The furnace temperatures are below the temperature limitations of conventional refractories of 1600 °C and above the minimum stable furnace temperature of 926 °C^[11].

The reaction furnace temperature should not exceed 1380 °C in order not to exceed the maximum temperature limitations of the equipment materials^[12].

In the Claus process, other sulfur compounds will form, such as carbon disulfide (CS_2) and carbon oxysulfide (COS), and these compounds can often contribute from 20 to 50% of the pollutants in the tail-gas^[13,14]. Furthermore, presence of O_2 traces in the CS_2 - H_2O mixture caused a decrease in the activity of alumina and titania catalysts due to sulfate formation^[15]. Therefore, COS and CS_2 should be hydrolyzed in the catalytic converter^[16,17], as shown below:



The temperature of the first catalytic reactor is maintained at about 350 °C to hydrolyze COS and CS_2 , while that of the subsequent reactors is just above the sulfur vapor dew point^[18]. Transition metal oxides can be used to modify gamma-alumina to form a catalyst that is effective at temperatures higher than the dew point of sulfur^[19-21]. However, thermodynamics provide a strong incentive to operate the catalytic converters at low temperature^[22,23] as a lower temperature should increase the exothermic reaction efficiency. Therefore, the temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is about 14-17 °C higher than the expected outlet sulfur dew point and High enough for hydrolysis of COS and CS_2 for the first catalytic converter only^[24] (about 350 °C).

In this paper, the temperature of reaction furnace of a typical clause sulfur recovery unit is adjusted to ensure suitable NH_3 destruction. Moreover, the inlet temperatures of SRU converters are determined such that the proper conversion can be achievable without any processing problems. The process temperatures are significant for designing a Claus sulfur recovery units.

SRU REACTION FURNACE

As mentioned before, since only one-third of H_2S convert to SO_2 in reaction furnace, the unreacted H_2S and inert gases consume the released energy from this exothermic reaction to reach the furnace temperature. It decreases the temperature of reaction furnace. For

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this reason, the gas streams containing considerable amounts of ammonia involve a split-flow reaction furnace design (Figure 2). In this method, all the combustion air and all the ammonia containing sour gas are mixed with a portion of the acid gas stream and inserted to the first zone of the furnace and the remaining acid gas is then mixed with the products of combustion from the first zone in zone 2 of the reaction furnace^[25,26].

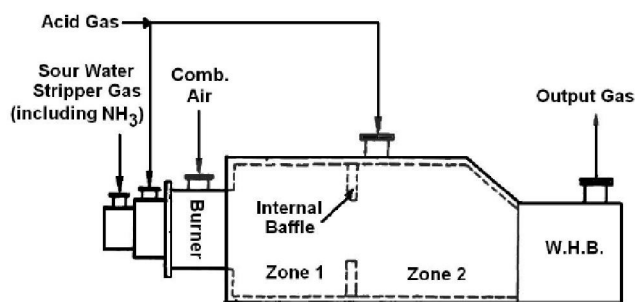


Figure 2 : A split-flow reaction furnace design

For illustrating the split-flow method, the Claus unit of a typical refinery is considered. The feed stock of this unit is consist of 74 Kmole/h acid gas from amine sweetening unit at 46 °C and 1.3 bar, together with 38 Kmole/h sour gas from sour water treating unit at 90 °C and 1.5 bar. The molar compositions of these streams are presented in TABLE 1. The sour gas stream contains 275.2 Kg/h ammonia and therefore, the furnace temperature should rise up to an appropriate value. For this reason, a case study is performed in which the acid gas split into two zone. Figure 3 illustrate the achieved result. The horizontal axis indicates the ratio between the flow rate of acid gas entered to zone 1 to the flow rate of acid gas entered to zone 2. The vertical axis represents the changes in the temperature of zone 1. This figure has a maximum which refer to the equilibrium reaction condition between air and H₂S. Before this point, the amounts of H₂S are less than needed one-third of total H₂S and therefore, temperature is decreased. Regarding to Figure 3, if the split-flow ratio was equal to 0.8, a temperature around 1350 °C would be achievable for zone1 of the reaction furnace. This temperature guaranties the complete destruction of NH₃. If more expensive refractories with more resistance was applied, the furnace would be operate at higher temperatures by decreasing this ratio (see figure 3).

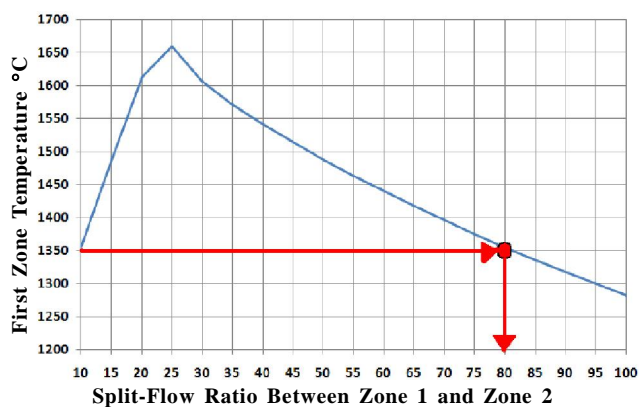


Figure 3 : A split-flow ratio between zone 1 and zone 2 vs. variations of zone 1 temperature

TABLE 1 : The composition of the Claus unit of a typical refinery

| Component | Mole Fraction | |
|-------------------------------|---------------|----------|
| | Acid Gas | Sour Gas |
| H ₂ S | 91.6 | 24.3 |
| H ₂ O | 7.3 | 33.2 |
| C ₂ H ₆ | 1.1 | 0 |
| NH ₃ | 0 | 42.5 |

Problems with the split-flow design include inadequate destruction of hydrocarbons and ammonia that might be contained in the bypassed portion of the acid gas and inadequate reaction furnace residence time for thermal Claus sulfur conversion. The alternate way to overcome this problem is preheating the acid gas and combustion air and using a high-intensity reaction furnace burner^[11].

SRU REACTORS (CONVERTERS)

The temperature of the process gas at the inlet of the catalytic converters should be such that the effluent gas temperature is about 14-17 °C higher than the expected outlet sulfur dew point. For this purpose, the outlet stream of two converters in the above plant is investigated. TABLE 2 presents pressure, temperature, and compositions of outlet streams of these converters. These data are achieved by the assumption of 265 °C for temperature of the first converter inlet stream and 195 °C for temperature of the second converter inlet stream.

Figure 4 present the variation of vapor phase fraction vs. outlet temperatures of two Claus reactors. According to this figure, dew point of the first converter

outlet stream is equal to 253 °C which is 57 °C less than its assumed temperature from TABLE 2. With respect to criterion of 14-17 °C, the temperature of 270 °C seems to be appropriate for the outlet temperature of first converter. However, this temperature should be increased to ensure hydrolysis of COS and CS₂ in the first reactor. Therefore, the assumption of 265 °C is a good value for the temperature of the first converter inlet stream. Furthermore, dew point of second converter outlet stream is equal to 210 °C which is 15 °C less than its assumed temperature value from TABLE 2 and takes the above criterion in the consideration.

TABLE 2 : The output conditions of Claus converters

| | Converter 1 | Converter 2 |
|-------------------|-------------|-------------|
| Pressure (bar) | 1.1 | 1.05 |
| Temperature (°C) | 310 | 225 |
| Component (mass%) | | |
| H ₂ S | 2.8 | 0.8 |
| H ₂ O | 22.9 | 28.0 |
| CO ₂ | 0.6 | 0.7 |
| SO ₂ | 2.7 | 0.8 |
| H ₂ | 0.2 | 0.2 |
| N ₂ | 56.4 | 65.7 |
| Sulfur | 14.4 | 3.8 |

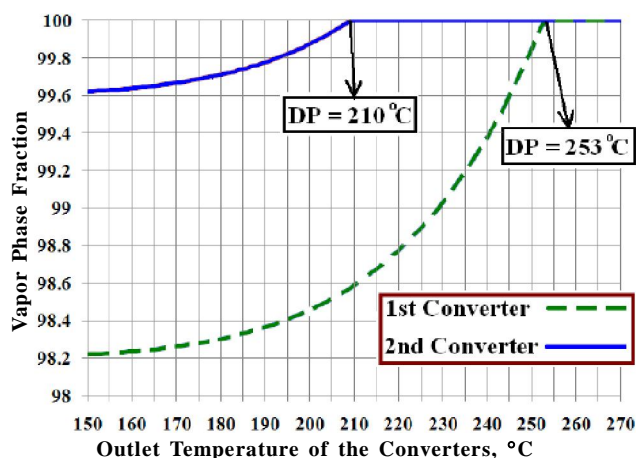


Figure 4 : Variation of vapor phase fraction vs. temperature, for two reactors outlet converters

CONCLUSION

The modified Claus process was introduced as a commonly unit to recover sulfur and destroy contaminants formed in upstream processing. In these units, in addition to converting H₂S to sulfur, other contami-

nants such as NH₃, CS₂, and COS must be eliminated. Rigorous adjustment of process temperatures is important for this subject. In this paper, the parameters that may affect adjusting the temperature of furnace and converters were investigated by means of analyzing a typical sulfur recovery unit. The achieved results illustrate a method which is useful for designing the new sulfur recovery units.

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